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(21) International Application Number: PCT/SE89/00125 (22) International Filing Date: 13 March 1989 (13.03.89) (31) Priority Application Number: 8800931-1 (32) Priority Date: 16 March 1988 (16.03.88) (33) Priority Country: SE (71) Applicant (for all designated States except US): TOUR & ANDERSSON AB [SE/SE]; Svärdlångsvägen 46, S-121 72 Johanneshov (SE). (72) Inventor; and (75) Inventor/Applicant (for US only) : KRÄMER, Johan [SE/SE]; Boråsvägen 11, S-520 30 Ljung (SE). (74) Agent: SIEBMANN, Hubertus; Götalands Patentbyrå AB, Box 154, S-561 22 Huskvarna (SE).		(81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BG, BJ (OAPI patent), BR, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CM (OAPI patent), DE, DE (European patent), DK, FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (European patent), NO, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US. Published <i>With international search report.</i> <i>In English translation (filed in Swedish).</i>
(54) Title: BRASS ALLOY AND PROCESS OF MAKING AND USE OF SAME		
(57) Abstract A brass alloy having the composition 63.5 - 66.5 % Cu + Ni, 0 - 0.8 % Ni, 0.5 - 3.0 % Pb, 0.3 - 1.0 % Si, preferably 0.65 - 0.80 % Si, 0.07 - 0.80 % Fe, preferably 0.10 - 0.50 % Fe and the rest mainly Zn. This alloy is resistant to dezincification, stress corrosion and intergranular corrosion. It can be formed by die-casting, chill casting, warm-pressing and hot-forging. Also, an alloy having a more limited composition 64.5 - 65.5 % Cu + Ni, 0-0.8 % Ni, 1.5 - 2.2 % Pb, 0.65 - 0.80 % Si, 0.10 - 0.20 % Fe and the rest essentially Zn can be extruded to bars, tubes and profiles. When the alloy is smelted, possible admixtures of Fe ought to be done in the form of a ferro-copper alloy.		

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Brass alloy and process of making and use of same.

The present invention relates to a brass alloy according to the preamble of patent claim 1. Furthermore, it relates to a method for the preparation of such a brass alloy according to the preamble of the first method claim as well as a use of said brass alloy.

Brass exists in two technically interesting main forms, α -brass containing more than 62 % Cu and $\alpha + \beta$ -brass containing 54-62 % Cu. The dividing line between α - and $\alpha + \beta$ -brass is located at 64.5 % Cu at the point of solidification of the alloy and at 62 % Cu at lower temperatures. By a slow cooling or a special heat treatment it is possible, if the percentage is above 62 % Cu, to recrystallize all the metal to the α -phase. The α -phase has a face-centered cubic structure, while the β -phase has a body-centered cubic structure. By adding other alloy metals said dividing lines can be moved somewhat. Such alloy metals are i.a. Sn, Pb, Fe, Ni, Mn, Si and Al, which may be included in various types of special brass.

As compared to pure copper the corrosion resistance of brass is reduced when the zinc content increases. This deterioration may in certain cases manifest itself as a selective elimination or corrosion of the zinc, a so called dezincification. In order to counteract this one or several inhibitors have been added to dezincification resistant brasses or special brasses. Said inhibitors may be plain or combined, e.g. P, As, Sb, Bi and/or Si. The α -phase is the only phase which can be inhibited by means of said elements. β -brass and the β -phase of a α / β -mixture are attacked firstly, since they are less electro-positive than the α -phase.

Also, brass can be subjected to other types of corrosion, such as stress corrosion and intergranular corrosion. Agents which prevent one type of corrosion are not always

effective against other types of corrosion.

The rest of the characteristics and possible disadvantages of the above-mentioned dezincification inhibitors may be summarized as follows:

P yields a hard brass; difficulties in adjusting the exact composition when smelting, due to pickling;

As may cause an intergranular corrosion in a sulphate-containing water;

Sb and Bi yield a brittle material and are usually avoided; and

Si does not display any particular negative characteristics and also results in stress corrosion resistance.

It has been held so far that other possibly existing alloy metals do not influence the power of dezincification resistance. Particularly, it has been held that Fe in this connection is an undesirable impurity and one has endeavoured to keep the iron content as low as possible. In those instances when iron in brass alloys has been included in a considerable amount, the purpose has been to increase the mechanical strength. In DIN 1785 for example a few brass alloys are mentioned as suitable corrosion resistant materials for condenser tubes in salt water, having the following percentages as to Cu, As, P and Fe:

CuZn30	Cu 70 (69-71 Cu)	As+P 0.020-0.035 Fe < 0.05
CuZn20Al	Cu 78 (76-79 Cu)	As 0.020-0.035 Fe < 0.07 As+P < 0.035
CuZn28Sn	Cu 71 (70-72.5 Cu)	As < 0.020-0.035 Fe < 0.07 As+P < 0.035

Applicant has proposed in SE-C-194 177 a dezincification resistant alloy having the following composition:

✓ Cu 64.5-66.5	percentage by weight	Al \leq 0.05	weight-% ✓
Mn 0.4-0.7	percentage by weight	Fe \leq 0.5	weight-%
✓ Pb 1.8-2.5	percentage by weight	Ni \leq 0.2	weight-%
✓ Si 0.5-0.8	percentage by weight	Sb \leq 0.05	weight-%
As 0.02-0.08	percentage by weight	Sn \leq 0.8	weight-%
		Zn	the rest

The percentages of Cu, Mn, Pb, Si, As and Zn are those percentages, which were regarded as fixing the characteristics of the prepared alloy. The percentages of the remaining elements Al, Fe, Ni, Sb, and Sn were values for a maximum admixture without any disturbing secondary effects. Thus, said elements were fundamentally undesirable impurities, which however could be put up with if present in the above-stated limited amount. The reason why said elements existed in Applicant's previous alloy is that brass to a great extent is made of brass scrap having a varying and partly unknown composition. By putting up with or tolerating more elevated impurity contents less expensive raw materials (scrap) could be used and consequently a reduced cost of production be attained.

Said previous alloy could solely be used when die-casting. By admixing lead it obtained excellent characteristics when machined in cutting processes. It displayed an excellent stress corrosion resistance as well as a satisfactory but limited dezincification resistance. However, it displayed an intergranular corrosion in a sulphate-containing water.

Consequently, the purpose of the developmental work, which resulted in the present invention, was to obtain a brass alloy having an intergranular corrosion resistance and an improved dezincification resistance as well as a maintained satisfactory stress corrosion resistance.

An additional purpose was to obtain a more generally useful brass alloy, which can be not only die-casted but also chilled, extruded to bars, tubes and profiles as well as warm-pressed. Additional desirable characteristics were satisfactory cold forming characteristics as well as maintained satisfactory characteristics when subjected to cutting operations.

We discovered then that the above-mentioned satisfactory characteristics could be obtained with an alloy having the following composition:

Cu	62.0-67.0	preferably	63.5-66.5	weight-%
Pb	0.5- 3.0	"	1.5-2,5	"
Si	0.3- 0.8	"	0.35-0.65	"
Fe	0.07- 0.8	"	0.10-0.50	"
Zn	the rest			

As much as 0.8 % Ni can replace Cu.

Brass having the lower Cu-content is solely dezincification resistant subsequent to a heat-treatment. The Cu-percentage ought to be larger than 62.5 % also when a heat-treatment is used.

In the developmental work it was assumed in the introductory phase that a maximum iron content of 0.5 % Fe could be tolerated. It was not assumed that there was a lower limit value. However, we found, when an accidental delivery of practically iron free raw materials was made, that a certain iron percentage is of crucial importance to the attainment of a dezincification resistance. The prepared alloy was completely devoid of a dezincification resistance. Continued developmental work proved that a satisfactory dezincification resistance and additional desirable characteristics were attained, provided the brass

alloy had the above-mentioned composition.

Previously corrosion resistant brass alloys having a Fe content as an active component have been proposed. US 2 007 008 relates to an alloy having the following composition: 61 % Cu, 0.4-0.8 % Si, 0.2-0.4 % Fe, the rest zinc. However, this alloy inevitably contains a certain amount of β -phase and consequently is not dezincification resistant.

DE 2 353 238 relates to an alloy having 95-63 % Cu, 0.04-0.25 % P, 0.07-0.7 % Fe and the rest Zn. Also, as much as 0.1 %, preferably 0.020-0.035 % As, can be added. As has been mentioned above, the phosphorus admixture yields a too hard product as far as many applications are concerned and there is a danger of smelting problems when a P-content is to be adjusted. An As-content results in an intergranular corrosion.

None of the known alloys contains lead and consequently they are not suitable for applications in cutting processes.

In addition to the elements mentioned the alloy according to the present invention may contain as much as 0.05 % Al, 0.8 %, preferably 0.5 %, Sn, 0.04 % P, 0.02 % Bi and 0.05 % Sb without a deterioration as regards the corrosion resistance and/or other characteristics of the alloy. In view of the risk of an intergranular corrosion in a sulphate-containing water merely traces of As ought to exist, say 0-0.020 % As, while in case this risk is smaller as much as 0.020 % As can be tolerated. As normally exists as an impurity in the brass raw materials in small amounts. Suppliers of brass from smelting plants do not warrant smaller amounts than 0.020 % As. An admixture of As of up to 0.020 % is regarded as an As-free material according to existing

regulations.

An additional purpose of the invention is to propose a method of producing a brass alloy of the type mentioned above, which enables one to use cheap brass scrap as a raw material.

This purpose is attained according to the invention in the following way. Initially pure copper, which the alloy possibly will contain, is melted and subsequently the brass scrap raw materials are added and melted and suitably finally possibly zinc. Subsequently the charge is analyzed and additional amounts of alloy metals are added to obtain the desired composition, Fe being added in the form of a master alloy, a ferro-copper alloy. A suitable ferro-copper alloy on the market contains 10 % Fe.

By admixing Fe as a master alloy, in which Fe as well as Cu are cubically face-centered, Fe will mainly be evenly distributed as finely divided Fe-atoms in the matrix of the material. In case Fe is added as Fe-metal, the iron will eagerly combine with e.g. Si, B, Al and P in the melt and form intermetallic inclusions with them. In that way the corrosion-inhibiting elements are combined and consequently they can no longer contribute to an increase in the corrosion resistance. Also, coarse, hard inclusions of this kind impair the cuttability due to the tool wear.

The invention will be explained in more detail by a few examples.

Example 1

An alloy designed for die-casting according to SE 194 177 was prepared with the following composition:

65.0 % Cu, 30.2 % Zn, 2.3 % Pb, 0.47 % Sn, 0.080 % As,
0.42 % Ni, 0.24 % Fe, 0.48 % Mn, 0.72 % Si, 0.01 % Al,

and <0.001 % P.

The alloy was moderately resistant to a dezincification.

Example 2

An alloy with the following composition was prepared:
64.9 % Cu, 32.3 % Zn, 1.7 % Pb, 0.033 % As, 0.54 % Si,
0.054 % Fe, 0.36 % Ni and 0.05 % Sn.

Despite the large percentage of As (0.033 %) (compared with the DIN-standard mentioned above) a pronounced dezincification of the alloy occurred.

Example 3

A representative example of the alloy according to the invention is:

64.6 % Cu, 31.2 % Zn, 2.0 % Pb, 0.70 % Si, 0.015 % As,
0.27 % Fe, 0.66 % Sn, 0.38 % Ni, 0.001 % Mn and 0.04 % Al.

This alloy has a satisfactory dezincification resistance, intergranular corrosion resistance and stress resistance. It is suitable for die-casting, extrusion, chill casting as well as warm-pressing.

Example 4

A specification as to bars and tubes according to the invention:

COMPOSITION

	Cu+Ni	Pb	Si	Sn	Fe	Mn	Ni	Al	Zn
	%	%	%	%	%	%	%	%	%
Min	64.0	1.5	0.65	-	0.10	-	-	-	-
Max	65.5	2.2	0.80	0.50	0.20	0.15	0.80	0.05	the rest

Fe is to be added in the form of a ferro-copper alloy (FeCu).

The rest of the impurities: max. 0.50 %.

PRODUCTION

The bars and the tubes respectively are pressed, heat-trea-

ted at $550 \pm 25^{\circ}\text{C}$ for 2 h, hard-drawn and reeled. It is easy to handle the bar products in a cutting operation and they have a satisfactory dezincification resistance, stress corrosion resistance as well as intergranular corrosion resistance.

Example 5

A specification as to the composition of billets designed for die-casting, chill casting or warm-pressing according to the invention.

	Cu+Ni %	Pb %	Si %	Sn %	Fe %	Mn %	Ni %	Al %	Zn %
Min	63.5	1.5	0.65	-	0.25	-	-	-	
Max	65.0	2.2	0.80	0.80	0.50	0.15	0.80	0.05	the rest

The rest of the impurities: max. 0.50 %

This alloy has a satisfactory dezincification resistance, stress corrosion resistance and intergranular corrosion resistance and it is easy to handle it in a cutting operation.

PATENT CLAIMS

1. A lead-containing brass alloy, characterized by the composition 62.0-67.0 % Cu+Ni, preferably 63.5-66.5 % Cu+Ni, 0-0.8 % Ni, 0.5-3.0 % Pb, preferably 1.5-2.5 % Pb, 0.3-1.0 % Si, preferably 0.65-0.80 % Si, 0.07-0.80 % Fe, preferably 0.10-0.50 % Fe and the rest mainly Zn.

2. A brass alloy according to patent claim 1, characterized in that it also contains 0-0.05 % Al, 0-0.8 % Sn, preferably 0-0.5 % Sn, 0-0.04 % P, 0-0.02 % Bi and/or 0-0.05 % Sb as well as not more than 0.50 % remaining elements.

3. A brass alloy according to patent claim 1 or 2, characterized in that it also contains 0-0.02 % As, preferably 0-0.02 % As.

4. A brass alloy according to patent claim 1, characterized by the composition 64.5-65.5 % Cu+Ni, 0-0.8 % Ni, 1.5-2.2 % Pb, 0.65-0.80 % Si, 0.10-0.20 % Fe and the rest mainly Zn.

5. A brass alloy according to claim 4, characterized in that it also contains 0-0.50 % Sn, 0-0.15 % Mn, 0-0.80 Ni, 0-0.05 % Al as well as not more than 0.50 % remaining elements.

6. A process for the preparation of an alloy according to any of patent claims 1-5, characterized in that initially pure copper, which may be an ingredient, is smelted and subsequently the brass scrap raw materials are added and smelted and possibly zinc, subsequent to which the charge is analyzed and additional amounts of alloy metals are added, until the desired composition is

attained, Fe being added in the form of a master alloy, as a ferro-copper alloy.

7. A use of the brass alloy according to any of patent claims 1-5, characterized in that it is used to prepare brass parts, designed to be employed in a corrosive environment at the risk of dezincification, stress corrosion and/or intergranular corrosion.

8. A use of a brass alloy according to patent claim 6, characterized in that a brass alloy having a composition according to any of patent claims 1-3 is used to prepare brass parts by die-casting, chill casting, extrusion or warm-pressing.

9. A use of a brass alloy according to patent claim 7, characterized in that a brass alloy having a composition according to patent claim 4 or 5 is used to prepare bar, tube or profile products.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/SE89/00125

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC 4 C 22 C 9/04, 1/02																										
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched 7</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border-right: 1px solid black; padding: 5px;">IPC 4</td> <td style="padding: 5px;">C 22 C 1/02, 9/04</td> </tr> <tr> <td style="border-right: 1px solid black; padding: 5px;">US C1</td> <td style="padding: 5px;">75: 157.5; 148: 434</td> </tr> </table> <p style="text-align: center; font-size: small;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *</p> <p style="text-align: center; padding: 10px 0;">SE, NO, DK, FI classes as above</p>			Classification System	Classification Symbols	IPC 4	C 22 C 1/02, 9/04	US C1	75: 157.5; 148: 434																		
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III. DOCUMENTS CONSIDERED TO BE RELEVANT * <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; font-size: small;">Category *</th> <th style="font-size: small;">Citation of Document, 11 with indication, where appropriate, of the relevant passages 12</th> <th style="width: 15%; font-size: small;">Relevant to Claim No. 13</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>US, A, 2 007 008 (HORACE A. STAPLES) 2 July 1935</td> <td style="text-align: center; vertical-align: top;">1-5,7-9</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>Patent Abstract of Japan, Vol 8, No. 19(C-207), abstract of JP 58-185738, publ.83-10-29</td> <td style="text-align: center; vertical-align: top;">1-5,7-9</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>Patent Abstract of Japan, Vol 8, No. 236, abstract of JP 59-118840, publ. 84-07-09</td> <td style="text-align: center; vertical-align: top;">1-5,7-9</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>Patent Abstract of Japan, Vol 126, No. C 249 , abstract of JP 59-118842, publ. 84-07-09</td> <td style="text-align: center; vertical-align: top;">1-5,7-9</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X A</td> <td>DE, A, 1 458 322 (AKTIESELSKABELT. NORDISKE KABEL- OG TRAADFABRIKER) 17 October 1968</td> <td style="text-align: center; vertical-align: top;">7-9 1-5</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X A</td> <td>DE, B1, 2 353 238 (WIELAND-WERKE AG) 6 February 1975 & FR, 2249173 GB, 1437056</td> <td style="text-align: center; vertical-align: top;">7-9 1-5</td> </tr> <tr> <td colspan="2" style="text-align: center; padding-top: 10px;">.../...</td> <td></td> </tr> </tbody> </table>			Category *	Citation of Document, 11 with indication, where appropriate, of the relevant passages 12	Relevant to Claim No. 13	X	US, A, 2 007 008 (HORACE A. STAPLES) 2 July 1935	1-5,7-9	X	Patent Abstract of Japan, Vol 8, No. 19(C-207), abstract of JP 58-185738, publ.83-10-29	1-5,7-9	X	Patent Abstract of Japan, Vol 8, No. 236, abstract of JP 59-118840, publ. 84-07-09	1-5,7-9	X	Patent Abstract of Japan, Vol 126, No. C 249 , abstract of JP 59-118842, publ. 84-07-09	1-5,7-9	X A	DE, A, 1 458 322 (AKTIESELSKABELT. NORDISKE KABEL- OG TRAADFABRIKER) 17 October 1968	7-9 1-5	X A	DE, B1, 2 353 238 (WIELAND-WERKE AG) 6 February 1975 & FR, 2249173 GB, 1437056	7-9 1-5	.../...		
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: 10</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>																										
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="text-align: center; padding: 5px;">1989-06-07</td> <td style="text-align: center; padding: 5px;">1989-06-14</td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;">International Searching Authority</td> <td style="border-bottom: 1px solid black; padding: 5px;">Signature of Authorized Officer</td> </tr> <tr> <td style="text-align: center; padding: 5px;">Swedish Patent Office</td> <td style="text-align: center; padding: 5px;"> Nils Engnell </td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	1989-06-07	1989-06-14	International Searching Authority	Signature of Authorized Officer	Swedish Patent Office	 Nils Engnell																
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

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A	DE, A, 2 040 031 (ALCUMA ESTABLISHMENT) 11 March 1971	1-9
A	Patent Abstract of Japan, Vol 8 No. 15 (C-206), abstract of JP 58-181839, publ.83-10-24	1-9